Original Research Article

Determination of Effective Calcium Carbonate Equivalence of Rice Husk Ash

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ABSTRACT

Rice husk ash is one of the widely available agricultural wastes in rice producing countries, with potential of replace limestone and also supply some of the nutrients which is beneficial for crop growth. There is little information on the effectiveness of rice husk ash for neutralizing acidity of soils. The design used in this study was completely randomized block design with 12 treatments and 3 replications. An incubation experiment was carried out in the Post graduate laboratory of Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore, India during Feb 2022 – March 2022. An incubation experiment was conducted to determine the percentage of effective calcium carbonate equivalence (ECCE) of rice husk ash (RHA) added to an agricultural loamy clay soil incubated for 1, 2, 3, 4 weeks which is acidic in nature and analyzed pH for each week interval. The result showed that after rice husk ash incorporation soil pH increased from acidic range to optimum level, but $CaCO_3$ in this study reacted faster compared to RHA because organic amendments decompose slowly compared to inorganic and ECCE also increased with incubation time. The rice husk ash containing calcium proved to be effective liming materials. The effect of rice husk ash needs longer time to react with soil than limestone and lasted longer compared to finely ground $CaCO_3$. The ECCE increased steadily after 10 and 20 weeks of incubation, now this study revealed its reaction only because of 4 weeks incubation times.

Keywords: *acid soil, rice husk ash, soil pH, soil amendment, neutralization of soil acidity*

1. INTRODUCTION

In India acid soils cover around 48 to 49 million hectares arable land of which 25 mha have pH below 5.5 and 23 mha have pH between 5.6 and 6.5, especially in Tamil Nādu around 4.85 mha [4]. Although we can't modify the acidic features of India's agricultural areas, the least we can do is make the soil suitable for agriculture. When soil shows low pH values (< 5.5), then the soil is called as acidic soil. Wherever rainfall exceeds evapotranspiration, bases such as calcium (Ca), magnesium (Mg), and potassium (K) (and salts) are displaced by H+ (derived from the dissolution of CO_2 in H_2O). The toxicity of aluminium (Al) and manganese (Mn), low pH, and deficits of certain important elements like as calcium (Ca), magnesium (Mg), phosphorus (P), boron (B), and molybdenum (Mo) are all major growth limiting factors in acid soil [13]. Liming with various liming materials is one way for acid soil management.

Rice husk ash is a common agricultural waste in rice-producing countries, with the ability to replace limestone and provide some nutrients that are favorable to crop growth. Rice husk is used as boiler fuel in rice mills which generate rice hush ash as a waste. In general, every 100 kg of husks burnt in a boiler will yield about 25 kg of RHA [5]. RHA is the most easily available forms among the other rice husk forms, because nowadays rice mills are emerging in every place and these rice husk converted into rice husk ash by the process of combustion.

Rice husk ash is alkaline in nature, which means it can raise the pH of an acidic soil, making it appropriate for crop production. Physical and chemical aspects of soil are essential agricultural phenomena that influence the soil's productive ability. Rice husk ash is a promising and environmentally favorable agricultural source. RHA not only adjust soil pH and also supply nutrients to crops because it contains CO_2 - 0.10%, SiO_2 - 89.90%, K_2O - 4.50%, P_2O_5 - 2.45%, CaO - 1.01%, MgO - 0.79%, Fe_2O_3 - 0.47%, Al_2O_3 - 0.46%, MnO - 0.14% [7]. It can also keep the soil's physical qualities, such as bulk density and total porosity, in good shape.

India has produced around 31 million tons of rice husk and thus generated 4.65 –5.58 million tons (15-18% of rice husk) of Rice Husk Ash (RHA) [8]. There are about 3000 modern rice mills in Tamil Nadu which generate considerable husk and rice husk ash every day (Source: TN rice mill owners association). Increased agricultural production generates quantities of agricultural waste from farms, and poor waste management leads to environmental problems. Hence utilization of such wastes not only benefits farmers but also our world.

Total calcium carbonate equivalence (TCCE) as estimated by titration method is rice husk ash capacity to neutralize acidity. The effective calcium carbonate equivalence (ECCE) is the fraction of TCCE that reacts with soil acidity during incubation with soil. The aim of this work is to determine ECCE of rice husk ash added to an acid soil.

2. MATERIAL AND METHODS

An incubation experiment was carried out in the Post graduate laboratory of Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore, India during Feb 2022 – March 2022, to study the effects on rice husk ash as an amendment for acid soil reclamation.

The soil of the incubation experiment was collected from experimental site in research farm of Horticultural Research Station, Woodhouse farm, Ooty, the Nilgiris district, India with a clay loam texture, which is acidic in nature. Soil samples were air dried, then ground to pass through a 2 mm sieve prior to analysis.

One hundred-gram of soil (oven-dry basis) was incubated in triplicate for 4 weeks with eight levels of reagent-grade $CaCO_3$ (0.0 (T_1), 0.5 (T_2),1 (T_3), 1.5 (T_4), 2.0 (T_5), 3.0 (T_6), 4.0 (T_7) and 5.0 (T_8) g kg^{-1} soil) and four rates of rice husk ash equivalent to 2.0, 3.0, 4.0 and 5.0 g $CaCO_3$ kg^{-1} soil. The rates (T_9, T_{10}, T_{11} and T_{12}) of rice husk ash (g kg-1 soil) were 37.6, 56.4, 75.2 and 94 (5% TCCE). The experimental units consisted of 12 treatments arranged in a completely randomized block design with three replications. The water content of the samples was adjusted to 70% of their water holding capacity. Moisture losses during incubation were replenished weekly with de-ionized water.

The ECCE of rice husk ash was derived from the relationship (cubic or quartic polynomial model) between the rates of pure calcium carbonate applied and pH after each of the four times of incubation. The ECCE values were expressed in percentage using the following equation:

$$\text{ECCE (\%)} = \frac{\text{ECCE Estimated (g CaCO3 kg}-1)}{\text{Amount rice husk ash (g kg}-1)} \times 100$$

2.1 Composition of rice husk ash

Rice husk ash were collected from Sneham rice mill, Pazhathara, Kerala. RHA pH is analyzed in 1:10 ratio (RHA: deionized water) by using pH meter. RHA were digested in Microwave digestion system (HNO_3: HCl: HF in 6: 2: 2 ratio) prior to analysis of C, Si, N, P, K, Ca, Mg, S, Na, Al, Cu, Fe, Mn and Zn content in ICP-OES instrument (Inductively Coupled Plasma Optical Emission Spectroscopy). Neutralizing value or TCCE of RHA is estimated by general titration method described by ISO 20978 using HCl and NaOH.

Table 1. Chemical composition of the rice husk ash used in this study

pH	NV	N	P	K	Si	Ca	Mg	S	Na	Al	Cu	Zn	Fe	Mn
								%						

8.3	**5**	**0.086**	**0.26**	**0.72**	**40.5**	**0.39**	**0.37**	**0.35**	**1.22**	**0.88**	**0.003**	**0.004**	**0.15**	**0.04**

NV- Neutralizing value

2.2. Analysis of soil

The soil samples to evaluate the effect of RHA as acidity corrective were collected in four different times. The pH analysis was performed at 7 days interval for 4 weeks after application of RHA. Soil pH was determined using deionized water in 1:2.5 ratio (soil: water).

TABLE 2: Initial soil properties used in incubation experiment

pH	**OC**	**Texture**	**N**	**P**	**K**	**Bulk density**	**Cu**	**Fe**	**Zn**	**Mn**	**S**
	%		Kg ha^{-1}			Mg m^{-3}	mg Kg^{-1}				
4.92	3	Clay loam	442	168	368	1.25	31.6	42.84	2.47	9.93	9.38

OC- Organic carbon

2.3 Statistical analysis

The data obtained from the experiment were subjected to statistical analysis using AGRESS software version 7.01. The level of significance used were $P < 0.05$. Critical difference (CD) values were calculated for the $P < 0.05$ whenever ''F'' test was found significant [8].

3. RESULTS AND DISCUSSION

3.1 Effect of Rice Husk Ash on Soil pH

The most important character of soil amendment is soil pH. In this pH of the RHA ash is 8.3 (Table 1). At 300-350^{o}C the destruction of cellulose and hemicellulose in rice husk produce organic acids and phenolic substances. After 350^{o}C, alkali salt separated in from those organic matrixes which in turn increase the pH of rice husk ash [9]. Thus, it proves that RHA would have an alkaline pH and its application will increase the soil pH. Rice husk ash were found to elevate the soil pH during the 4 weeks of incubation (Table 3:). Initial soil pH is increased after rice husk ash application from 4.92 to 5.67 at highest dose applied in the I week sampling.

In the sampling II weeks after RHA application, the increase was clearest in soil in which the pH reached a value of 5.68 at the highest dose applied (T_{12}), and less pronounced in the lowest dose applied (T_9) where RHA dosage induced a pH of 5.47. [2, 10, 11, 12] reported similar result that rice husk ash increased the soil pH but it required more time for faster reaction.

TABLE 3: Effect of Rice Husk Ash on Soil pH

Treatments	I week	II week	III week	IV Week
T_1	5.28	5.26	5.25	5.30
T_2	5.39	5.43	5.47	5.52
T_3	5.50	5.53	5.60	5.64
T_4	5.62	5.64	5.80	5.84
T_5	5.84	5.87	5.89	5.93
T_6	6.04	6.11	6.17	6.25
T_7	6.28	6.30	6.34	6.37
T_8	6.45	6.44	6.50	6.53
T_9	5.45	5.47	5.50	5.52
T_{10}	5.50	5.52	5.55	5.61
T_{11}	5.57	5.59	5.65	5.69
T_{12}	5.67	5.68	5.70	5.72
MEAN	5.72	5.74	5.79	5.83
SEd	0.0459	0.0426	0.0456	0.0280
CD	0.0948	0.0878	0.0941	0.0578

SEd – Standard error of difference, CD – Critical difference

3.2 Effective Calcium Carbonate Equivalent of Rice Husk Ash

The best-fit regression model to predict ECCE after 2 week of incubation time is cubic as shown in Fig. 1. The pH values for RHA at T9, T10, T11 and T12 were 5.47, 5.52, 5.59 and 5.68 corresponding to ECCE of 0.7, 0.9, 1.2 and 1.5 g CaCO3 kg-1 soil or 1.86%, 1,59%, 1,59% and 1.59% on ECCE % of RHA basis respectively.

The ECCE (g CaCO3 kg-1 soil) increases with incubation time and higher dose applied but it needs time to react in soil until reaction is not steady (Fig. 2). After 2 week of incubation the ECCE was around two times lower than TCCE provided by RHA (i.e., 1.5-2.0 % g kg^{-1}).

The high organic matter content of RHA (44-52%) seems to reduce the efficiency of RHA calcium carbonate, hence their ECCE, at the beginning of incubation. This is attributable to greater mineralization of by-product organic matter early in the incubation period [3]. Indeed, the efficiency of RHA to neutralize soil acidity decreased in the following order: T_{12} > T_{11} > T_{10} > T_9 (Fig. 2). The ECCE of DPS after 2 weeks of incubation were 0.5-0.6 for T_9, 0.8 for T_{10}, 1.2 for T_{11} and 1.4 for T_{12} (Fig. 2) and corresponded respectively to 5% of TCCE. Rice husk ash serves as a corrective of soil acidity, but has a low effective calcium carbonate equivalent (around 3 %) [2].

Figure 1. Relationship between $CaCO_3$ added to soil and pH of CaCO3-amended soil after two weeks of incubation.

Figure 2. Estimated effective $CaCO_3$ equivalence of RHA as a function of incubation time.

4. Conclusion

Rice husk ash were effective liming materials for acid soil. Expressed as percentage, the ECCE increased after 2 weeks of incubation according to dose applied. Higher RHA dose applied reacts faster compared to lower dose and gave increased ECCE but clear results only obtained after 10 weeks of incubation according to [1]. For maximum effectiveness RHA several months would be necessary to allow sufficient time for RHA to react with soil. The effect of rice husk ash needs longer time to react with soil than limestone and lasted longer compared to finely ground $CaCO_3$. The ECCE increased steadily after 10 and 20 weeks of incubation, now this study revealed its reaction only because of 4 weeks incubation times.

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